

SOME EFFECTS OF SURFACE MODIFICATION
OF STARCH GRANULES BY IODINE

by

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TABLE OF CONTENTS

INTRODUCTION	1
LITERATURE SURVEY	4
EXPERIMENTAL PROCEDURE	7
Preparation of Starch	7
Determination of Adsorption Capacity	8
Preparation of Starch-Iodine Complexes	9
Removal of Iodine with Ammonia in CCl_4	10
Purification of Deiodized Samples	11
Methods of Analysis	12
RESULTS AND CONCLUSIONS	20
SUMMARY	28
ACKNOWLEDGMENTS	30
LITERATURE CITED	31

INTRODUCTION

Starch is a material which has been recognized and used since very early times. This might naturally be expected since starch can be obtained directly from certain roots and cereals, and since it is obviously adapted for use as food, adhesive, etc.

The first description of the preparation of starch is given by Cato (1) about 170 B. C. in his treatise on Roman agriculture. Despite this early knowledge of starch manufacture there was only a very gradual development during the succeeding 2000 years. The manufacture of starch did not become of industrial importance until about the middle of the last century. The discovery of starch sugar by Kirckhoff in 1811 and the practical application of "roasted starch" by an English calico printer about 1821 mark important stages in the development and expansion of this industry (2). As the epochal discovery of Kirckhoff marked the inception of true scientific investigations in this field, and at the same time contributed significantly to the expansion of the starch manufacturing industry, 1821 marks the beginning of modern starch chemistry.

In spite of the fact that scientific research has been continuously carried out since this date by hundreds of workers, starch is still the subject of a great deal of controversy, especially in regard to its gross physical structure.

It is agreed that dispersed starch contains two carbohydrate substances, both polymers of glucose, but differing in structure

and properties. The minor fraction, amylose, is a linear polymer linked through 1,4- α -glucosidic linkages, while in the major fraction, amylopectin, the linear chain is interrupted by branching through 1,6- α -glucosidic linkages. There is, however, some question whether the fraction, amylose, exists in granular starch *per se* or whether the granular starch is composed of only the one carbohydrate substance, amylopectin. However, it can be said that the starch granule is composed of an association of starch molecules varying in size, shape, and degree of branching. Other than this there is very little agreement among various workers on the gross structure of the starch granule.

As the principal source of starch is corn, it would be of great benefit to the states lying in the corn belt if the demand for starch could be materially increased. Aside from a small demand for powdered and pearl variety, starch at the present time is being utilized chiefly for the production of sugars, syrups, pastes, and colors; and while the market for these products will probably continue at the present level or rise somewhat, other outlets must be found if the demand for starch is to rise enough to benefit the corn states.

One of the most logical paths to follow would be the conversion of starch into useful derivatives, which could be used as a source of new chemical products, or a cheaper source of chemicals now on the market. However, with the exception of some esters and ethers which are of little industrial importance, few derivatives of starch have been known until just recently.

The direct chlorination of starch by the use of liquid chlorine was developed at this laboratory (3) and starch chlorides of high molecular weight have been prepared. These starch chlorides offer one of the most promising outlets for the utilization of starch.

It has been found, though, in the course of this work, as in work done in the past, that the reactivity of the starch, and also that of the products derived from it, is dependent upon the source and past history of the granule. Additional information on the gross structure of the starch granule, especially the relative importance of the granule surface to the interior structure of the granule, is needed. It was for this purpose that this problem was undertaken.

The method of attack chosen was the well-known starch iodine reaction. The procedures followed were essentially the same as those used in previous starch-iodine studies at this laboratory (4).

Iodine was adsorbed on or into the starch granules from an iodine-carbontetrachloride solution, and the adsorbed iodine was reacted in situ with ammonia to form nitrogen triiodide. This nitrogen triiodide which is highly unstable at room temperature is presumed to have decomposed violently and in so doing modified the surface and gross structure of the starch granule to a degree dependent upon the location and amount of adsorbed iodine. In the present work, it was planned that the amount of adsorbed iodine be kept low so that the resulting modification be limited primarily to the surface. It was the further purpose of this

work to study the effects of such modification upon various types of starch, both native and those modified by various degrees of solvent extraction, with regard to the amount of iodine adsorbed, viscosity, and alkali liability.

LITERATURE SURVEY

The starch iodine reaction has been the subject of much research. Many workers have been of the opinion that if the starch iodine reaction were more fully understood, it would furnish the key to the gross structure of the starch granule.

Colin and de Claubry (5) first studied the reaction in 1814. They reported that the addition of iodine to dispersed starch resulted in a violet. blue or bluish black color which was characteristic of all starches. The literature since that date has been full of conflicting data, mostly pertaining to starch in the dispersed state.

The first major question to arise involved the nature of the starch iodide complex, whether it was simply an adsorption phenomenon or whether it had a definite molecular formula.

Jaquelain (6) as early as 1840 stated that the starch iodide combination was not a chemical phenomenon. Schoenbein (7), as well as Kemper (8), Rouvier (9), Sonstadt (10), and Euler and Myrback (11), believed on the other hand that the combination formed a very definite chemical compound.

Duclaux (12) believed the formation of starch iodide to be a simple case of molecular adhesion without a constant compo-

sition, and that its formation was dependent upon an equilibrium between water, starch, and iodine.

Mylius (13) presented evidence that the starch iodide was an individual compound and not a mixture, while Kuster (14) reported it to be a well-defined, solid solution of iodine in starch. Roncato (15) in 1924 found that starch iodide showed the same ultra violet spectrum as starch itself, indicating thereby that no chemical change was involved in the formation of the complex.

A second major question which arose involved the origin of the blue color.

Guibort (16) found that the outer coating and inner soluble matter of the starch granule were colored equally by iodine. Naegeli (17) reported, however, that by treatment with dilute acids in the cold, starch may be separated principally into two modifications, one of which was soluble in water and gave a blue iodine coloration, the other being insoluble in water and giving a yellow iodine coloration. The latter constituted the hull substance of the granule. The two modifications did not occur as distinct entities but were connected in transition stages by intermediate compounds.

Leroy (18) concluded that water was necessary for the coloration, while Tinkler (19) reported a per iodide necessary. Angelescu and Mirescu (20) considered potassium iodide essential.

Colors other than blue, violet, and black have been reported for the starch iodide. Kreusler and Dafert (21) discovered a starch giving a red color with iodine. Dubosc (22) believed

iodine vapors produced markedly varied colorations with starches of different origins. Fresenius (23) found that the intensity of the color of the complex was dependent upon the temperature. M. Samec (24) decided that the color was dependent on mean molecular size.

There are few references in the literature on the use of granular starch to form the starch-iodide complex, a phase related to the present work.

Berczeller (25) found evidence that iodine is not adsorbed by starch from a carbontetrachloride solution. Hallgrew (26), however, found that starch adsorbed iodine from an ether solution.

Euler and Bergman (27) used benzene as a solvent, and found a definite break in the adsorption curve. They believed, however, that this indicated the formation of two chemical compounds.

McCaskill (4) succeeded in adsorbing as much as 30 per cent iodine into starch from a carbontetrachloride solution, and in modifying markedly the structure of the starch by removing the adsorbed iodine by reaction with ammonia.

Although much of the literature seems confusing and conflicting, it must be remembered that starch is a very complex substance, especially in the dispersed state. It has been only in recent years that sufficient information has been acquired to enable present investigators to interpret the results obtained by early workers.

EXPERIMENTAL PROCEDURE

Preparation of Starch

In this work it was decided to use both native and solvent extracted starches, since it has been found in previous work that the solvent extraction of naturally occurring substances alters the pasting characteristics and also the alkaline number of a starch.

In all, three different starches, two corn and one glutinous sorghum, were used.

The first cornstarch with the laboratory designation cornstarch No. 8 was obtained from the Baker and Adams' Company on February 18, 1949. The second, designated cornstarch No. 10, was obtained from the Penick and Ford Company on August 16, 1950. The glutinous sorghum starch, designated G. S., was received from the Hubinger Company on August 30, 1950. Each of these starches was carefully blended, sealed in glass jars, and stored in a cold room at a temperature of 4° C. until used.

Essentially, the procedure used for solvent extraction was that recommended by Schock (28), whereby an aqueous hydrophilic solvent is used for the removal of lipoid material from starch. Five hundred grams, calculated on a dry weight basis, of each of the starches were suspended in three parts by weight of 85 per cent (by volume) aqueous methanol. The slurry was refluxed with agitation for five two-hour periods. At the end of each two-hour period, the samples were filtered by suction and resuspended in

fresh solvent. After 10 hours, the samples were filtered and washed free of methanol by repeated slurring with cold, distilled water. The methanol was considered removed when its odor could no longer be detected in the moist samples. The extracted samples were air dried at room temperature for a period of 24 hours, and then ground just to the point where sifting through a 60 mesh sieve was possible. These samples were designated 8E, 10E, and G.S.-E respectively. Samples were removed from each lot for moisture determinations, and the remainder stored in tightly closed jars.

An additional 500 grams of cornstarch No. 10 (dry weight basis) after being subjected to the standard extraction above was further extracted. The sample was resuspended in 3 parts by weight 85 per cent (by volume) aqueous methanol and refluxed with agitation for a 24-hour period. The sample after being filtered by suction was resuspended in 3 parts by weight absolute methanol and again refluxed with agitation for an additional 24 hours. The sample was then filtered, washed free of methanol, and air dried 24 hours at room temperature. After sifting through a 60 mesh sieve this sample was designated 10EEE.

Determination of Adsorption Capacity

A number of five gram samples, calculated on a dry weight basis, of each of the various starches were placed in 250 ml iodine flasks. To each flask was added 100 ml of an iodine-carbontetrachloride solution ranging in concentration from 0.2 g

to 2.4 g of iodine per 100 ml of solution. These concentrations varied by increments of 0.2 g iodine, and were obtained by diluting a stock solution containing 24 g of iodine per liter. Each sample was then agitated at room temperature for a period of 24 hours, at the end of which they were filtered, washed free of excess iodine with carbontetrachloride and air dried. The iodine content of each sample was determined by the sodium peroxide fusion method, and the results plotted to obtain the curves shown in Figs. 1, 2, and 3.

Preparation of the Starch-Iodine Complexes

For each starch a number of points were chosen from its adsorption curve. For all of the starches used, one of these points corresponded to a concentration of 2.4 g iodine per 100 ml of solution. Another corresponded to the concentration where the lower level of the adsorption curve first broke. This latter concentration varied from one starch to another. For cornstarch Nos. 8, 8E, G.S., and G.S.-E, it represented a concentration of 1.4 g iodine per 100 ml of solution. For cornstarches Nos. 10, 10E, and 10EEE, it represented a concentration of 0.8 g of iodine per 100 ml of solution. Also for starches Nos. 10, 10E, 10EEE, G.S., and G.S.-E, a third point was chosen at a concentration of 0.1 g of iodine per 100 ml of solution, and for starch No. 10 an additional one at concentration of 0.2 g of iodine per 100 ml of solution was taken.

For each point chosen on the adsorption curve a 75 g sample

(dry weight basis) of each starch was placed in a 3-liter round-bottom flask. A volume of 1500 ml of an iodine-carbontetrachloride solution of the required concentration was added and the mixture agitated at room temperature for 24 hours. At the end of this time, the sample was filtered by suction, washed free of excess iodine with carbontetrachloride, and air dried.

The iodine content of each sample was determined by the sodium peroxide fusion method. In all cases the iodine content was found to be the same within experimental error as that indicated by the adsorption curve.

These starch-iodine complexes were then stored in tightly covered glass bottles.

Removal of Iodine with Ammonia in CCl_4

On the basis of previous work done in this laboratory, carbontetrachloride was chosen as the medium in which the starch-iodine complexes were suspended for iodine removal by ammonia. It was found that there was less trouble from iodoform and other iodide-containing products, which might be formed during the course of the reaction, when inert carbontetrachloride was used instead of ethanol or methanol.

Each starch-iodine complex sample was placed in a 5-neck 250 ml flask, and 150 ml of redistilled carbontetrachloride was added. An ammonia outlet, stirrer and condenser were connected, and ammonia gas was bubbled in until the sample turned white. This required on the average about 15 to 30 minutes. The sample

was then filtered on a sintered glass funnel, washed thoroughly with carbontetrachloride, and briefly air dried.

Purification of Deiodized Samples

Since any iodide-containing compound in the deiodized samples would materially affect the pasting characteristics of the starches, it was necessary to remove completely any such compounds. As it was desired to avoid the use of water because of its known effects on the granule, a solvent had to be used that was non-aqueous, polar, and of low molecular weight. Also, it was desired to avoid high temperature; therefore hot Soxhlet extractions were not advisable. It was found that these iodides could best be removed by slurring the deiodized sample with cold, absolute methanol for an extended period of time.

Each deiodized sample was placed in a 500 ml round bottom flask, and approximately 350 ml of cold, absolute methanol added.

The sample was then stirred for eight 12-hour periods. At the end of each 12-hour period the sample was filtered and re-suspended in fresh solvent. After the eighth period the sample was filtered, air dried at room temperature for 24 hours, and ground sufficiently to enable it to pass through a 60 mesh sieve. Each sample was then tested for any remaining iodine or iodides by the sodium peroxide fusion method.

To determine the effect of the prolonged immersion of the native starches in the cold absolute methanol, samples of corn-starch No. 10 and the glutinous starch were subjected to the same

treatment described above, and the effects on the pasting characteristics and alkali liability numbers of the starches were noted. The results are given in Tables 1 and 2.

Methods of Analysis

Iodine Content. The iodine contents of the various samples were determined by using the sodium peroxide fusion method. To reduce any possible error, a five ml micro burette was used for all titrations. The results are shown in Table 1, and the adsorption capacity curves are shown in Figs. 1, 2, and 3.

Viscosity. The viscosity records and certain other characteristics of the original starches, and starch samples prepared from them by the adsorption and spontaneous removal of iodine, were determined by means of a viscometer designed and built in this laboratory (29). The viscosity curves for starches 10, 10E, 10EEE, G.S., and G.S.-E are shown in Figs. 4 and 5, respectively. The values for the others are recorded in Table 2.

Alkali Number. Alkali numbers were determined using the Schock method (28), with the modifications suggested by Baldwin (30). The values are recorded in Table 1.

Table 1. Concentration of iodine-carbontetrachloride solutions, iodine content, and alkaline number of products produced.

Sample number	: Concentration : : solution*	Per cent : iodine	: Alkaline : number
Cornstarch No. 8			
Original No. 8	0.0	0.000	9.46
1-J(I)-6b	1.4	0.254	9.86
1-J(I)-1b	2.4	0.794	10.55
Cornstarch No. 8E			
Starch No. 8E	0.0	0.000	10.21
4-J(I)-6c	1.4	0.253	10.76
4-J(I)-1c	2.4	0.759	11.27
Cornstarch No. 10			
Original No. 10	0.0	0.000	9.59
5-J(I)-13A	0.1	0.629	9.84
5-J(I)-12A	0.2	0.640	7.77
5-J(I)-9A	0.8	0.733	10.11
5-J(I)-1A	2.4	1.42	10.84
Cornstarch No. 10E			
Starch No. 10E	0.0	0.000	10.06
6-J(I)-13A	0.1	0.452	10.56
6-J(I)-9A	0.8	0.508	11.41
6-J(I)-1A	2.4	1.013	11.81
Cornstarch No. 10EEE			
Starch No. 10EEE	0.0	0.000	10.33
7-J(I)-13A	0.1	0.308	10.63
7-J(I)-9A	0.8	0.325	12.23
7-J(I)-1A	2.4	0.761	12.98
Glutinous starch			
Original G.S.	0.0	0.000	5.19
8-J(I)-13A	0.1	0.051	5.32
8-J(I)-6A	1.4	0.354	6.91
8-J(I)-1A	2.4	0.710	7.12
G.S.-E			
G.S.-E	0.0	0.000	4.99
9-J(I)-13A	0.1	0.082	5.48
9-J(I)-6A	1.4	0.394	8.25
9-J(I)-1A	2.4	0.765	8.67

* Concentration given in grams of iodine per 100 ml of solution.

Table 2. The hot peak (w_1), the cold peak (w_2), the ratio w_2/w_1 , gel strength, and the ratio $(GS-w_2)/w_2 \times 100$ of the various products.

Sample number	w_1	w_2	w_2/w_1	G.S.	$\frac{GS-w_2}{w_2} \times 100$
Cornstarch No. 8					
Original No. 8	376	1341	3.57	1874	39.7
1-J(I)-6b	310	1460	4.71	1075	-26.4
1-J(I)-1b	280	1436	5.74	1092	-23.9
Cornstarch No. 8E					
Starch No. 8E	337	1700	5.04	1577	7.6
4-J(I)-6c	252	1556	6.17	1062	-31.7
4-J(I)-1c	189	1126	5.96	924	-17.9
Cornstarch No. 10					
Original No. 10	383	1620	4.23	2619	61.7
5-J(I)-13A	280	1674	6.26	1125	-32.8
5-J(I)-12A	335	1598	4.77	2050	28.2
5-J(I)-9A	204	1307	6.41	863	-33.2
5-J(I)-1A	117	960	8.21	612	-36.2
Cornstarch No. 10E					
Starch No. 10E	317	1843	5.81	1904	3.3
6-J(I)-13A	192	1382	7.20	1194	-13.6
6-J(I)-9A	186	1430	7.69	847	-40.8
6-J(I)-1A	140	1248	8.91	778	-37.7
Cornstarch No. 10EEE					
Starch No. 10EEE	278	1643	5.71	1238	-24.7
7-J(I)-13A	189	1187	6.28	1173	-1.2
7-J(I)-9A	187	1342	7.18	1021	-23.9
7-J(I)-1A	127	1218	9.59	723	-40.6
Glutinous starch					
Original G.S.	216	214	0.99	139	-35.0
8-J(I)-13A	295	229	0.78	79	-65.5
8-J(I)-6A	176	115	0.67	33	-71.3
8-J(I)-1A	136	88	0.65	40	-54.5
G.S.-E					
G.S.-E	366	295	0.81	158	-46.5
9-J(I)-13A	249	166	0.670	43	-74.0
9-J(I)-6A	100	60	0.50	20	-60.0
9-J(I)-1A	83	35	0.42	5	-85.7
Samples extracted in cold methanol					
Cornstarch No. 10	357	1778	4.98	2200	23.1
G.S.	366	282	0.77	194	-45.4

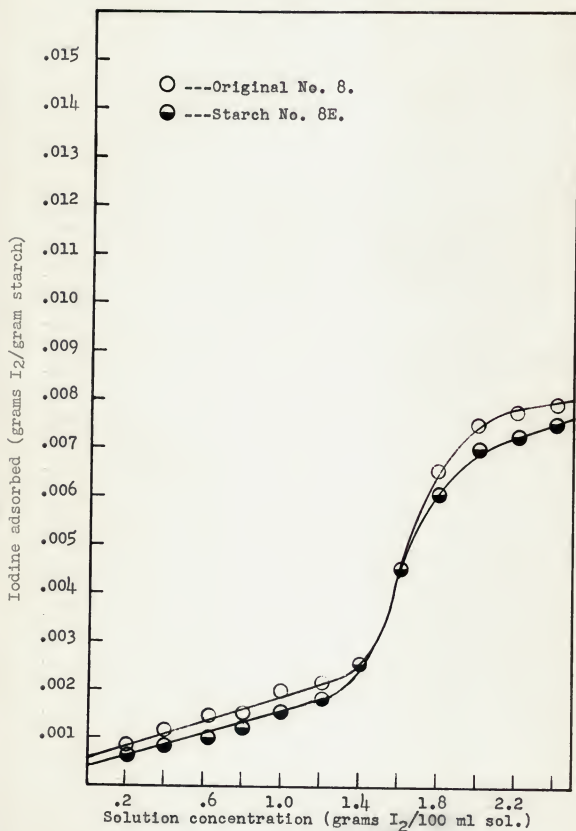


Fig. 1. The adsorption curves Cornstarch No. 8 series.

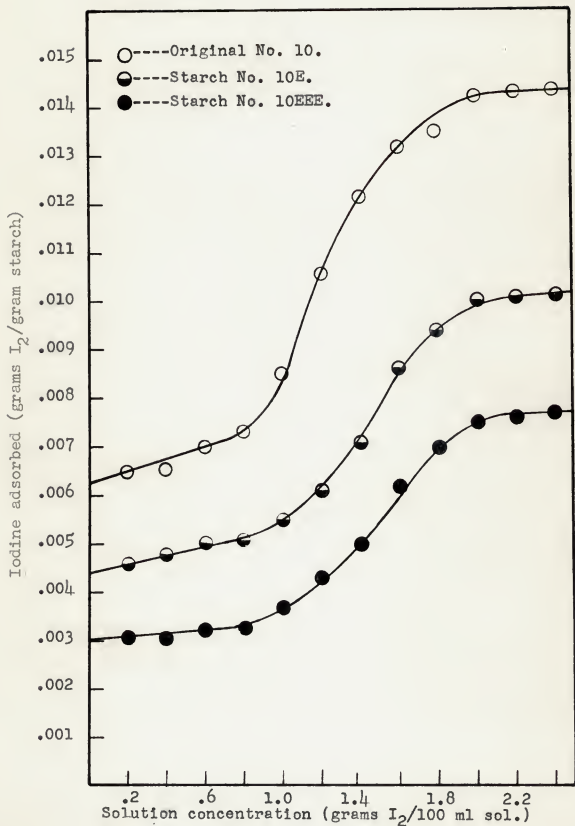


Fig. 2. The adsorption curves Cornstarch No. 10 series.

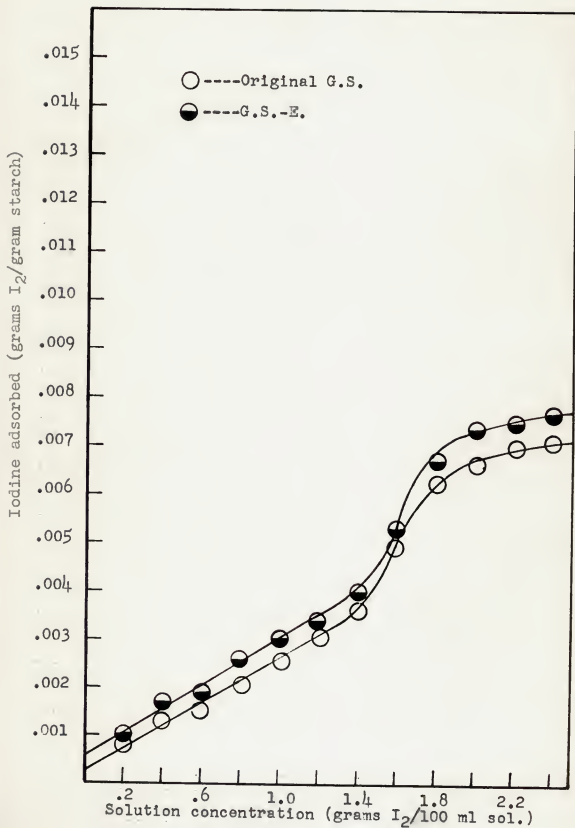


Fig. 3. The adsorption curves G.S. series.

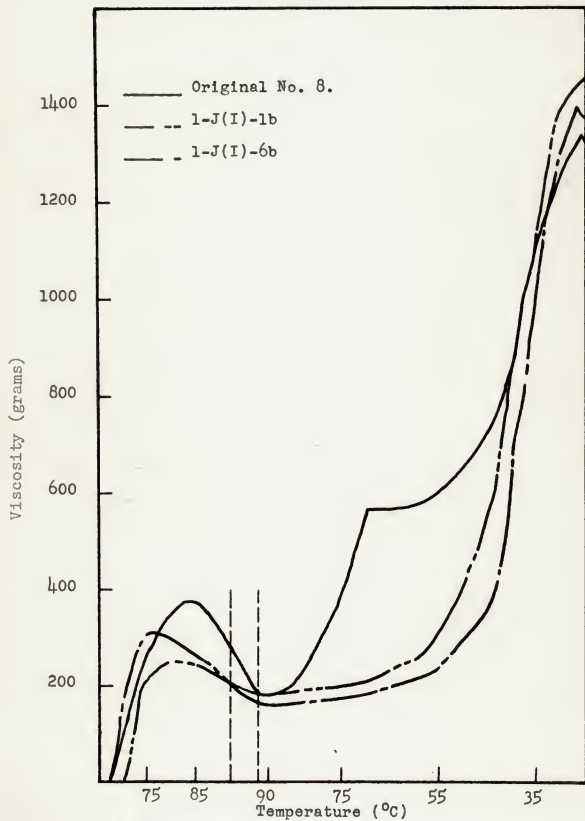


Fig. 4. The viscosity curves Cornstarch No. 8 series.

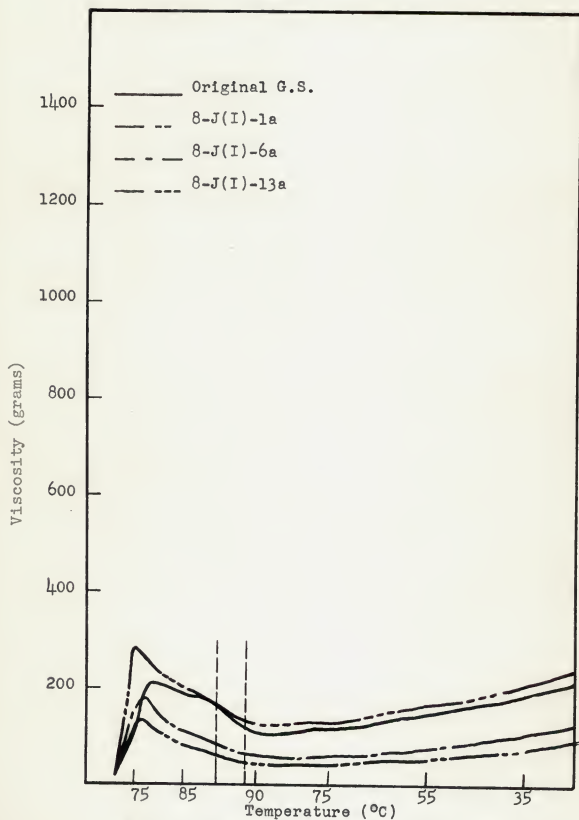


Fig. 5. The viscosity curves G.S. series.

RESULTS AND CONCLUSIONS

On the basis of the properties of recoverable molecules from aqueous starch dispersions, the starch granule may be considered an association of starch molecules varying in size, shape, and degree of branching. Further, it is believed that such an association results from intermolecular attraction made possible through hydrogen bonds. It should be pointed out, however, that there is no direct evidence for the existence of molecules in the granule. There is a definite possibility that a relatively few exist, but there is evidence that more segments or fragments which could be considered as molecules are produced during gelatinization.

Previous experimental evidence has indicated that the polymeric segments of the granule exist in a more or less strained condition, and if allowed, would relax into a helical form corresponding to the lowest energy state. Each turn of the helix would possess six glucose units. This relaxation is prevented, however, by branching and intermolecular association. Facts suggest that the dominating structure in the granule is one in which a number of extended segments are associated. This structure might be regarded as a multiple helix (31).

In this work it was found that, with increased time of solvent extraction, the amount of iodine adsorbed by the non-glutinous starches decreased. Within the cornstarch No. 10 series, the amount adsorbed from the most concentrated solution used, 2.4 g iodine per 100 ml of solution, decreased from 0.0142 g iodine per gram starch for the original to 0.01015 g iodine per

gram starch for the standard extracted 10E; there was a further decrease to 0.00761 g iodine per gram of starch for the exhaustively extracted 10EEE. A similar but smaller decrease was observed for the cornstarch No. 8 series. This behavior of a given starch together with the small amounts of iodine adsorbed, the size of the iodine molecule, the change in the quality of color with iodine adsorption, and effects on viscosity characteristics and alkali lability, suggests that solvent extraction progressively constricts and randomizes the granular surface, accompanied with increased formalization of the internal structure of the granule.

It is generally recognized that the length of an α -glucopyranose polymer must be at least that of six glucose units in order to possess an induced dipole of sufficient strength to form the starch iodine complex. Constriction and randomization of the granular surface would tend to obstruct the formation of the formalized iodine complex; the attendant range of color would be from the characteristic blue to that of molecular iodine, as is shown in Table 3. There is considerable evidence also that the indicated surface changes are facilitated and accompanied by changes in internal structure arising from the removal of naturally occurring substances from within the granule and from the protracted action of diffusing, low molecular weight polar solvent molecules. The removal of adsorbed substances from within the granule, and the prolonged action of a hydrogen bond breaker, such as methanol, would permit the normally strained and extended

helix to relax with the resulting development of increased internal structure. That the effects of solvent extractions do not include depolymerization either in the surface or within the granule, due to the rupture of primary bonds, is indicated by viscosity and alkali number measurements. Chemical depolymerization, which would mean a deep-seated structural injury, would have resulted in a pronounced loss in viscosity, and a marked increase in alkali consumption.

The adsorption capacity of the glutinous starch, as was expected in view of the above, increased through solvent extraction. It is agreed that the structure of glutinous starch is more random than that of non-glutinous starch and as a result, the former would be less likely to undergo an increase in internal structure through solvent extraction. The extraction would strip the granule of any surface lipids and thus increase or open the available surface to the iodine. The viscosity curves and the alkali numbers appear to confirm this point of view.

The colors of the starch iodine complexes for a given starch were changed markedly by solvent extraction. These are shown in Table 3.

The color was not indicative of the amount of iodine adsorbed, for the yellow No. 10EEE complex actually contained more iodine than did the purple No. 8 complex. Exhaustive extraction of the non-glutinous starch resulted in a complex of similar color to that obtained by standard extraction of the glutinous starch.

Table 3. Colors of the starch-iodide complexes formed from iodine solution containing 2.4 grams iodine per 100 ml solution.

Sample	Color
8	Violet
8E	Blue-violet
10	Purple
10E	Blue
10EEE	Yellow
G.S.	Brown-yellow
G.S.-E	Yellow

Barham and Campbell (32) found that solvent extraction of non-glutinous starches had several effects on their viscosities. After extraction, gelatinization began at a lower temperature, and the viscosity increased more rapidly to the maximum; the decrease in viscosity during cooking was less, and increase during cooling was much more rapid; and, the plateau was absent and the maximum was much higher. Here, exhaustive extraction carried these effects still further. The extraction of No. 10 starch with cold methanol alone, as shown in Table 2, produced an effect which lay between the original starch and the standard extracted No. 10E. This would indicate that part of the lipids are located on or near the granule surface, where they are easily removed even by cold methanol. These surface lipids are important in that they can serve to inhibit the pasting characteristics of a starch. But the most of the lipids are located within the granule and require hot methanol for removal.

With the glutinous starch, solvent extraction raised both the

hot peak, w_1 , and the cold peak, w_2 . It also increased the numerical value of the ratio w_2/w_1 . From this it was assumed that the glutinous starch had most of its lipids located on the granule surface, where they were easily removed without causing an important increase in granular structure. After removal of these surface lipids the water was able to diffuse more evenly throughout the granule during the pasting. Extraction of the glutinous starch with cold methanol, which produced a starch with almost identical pasting properties of the standard extracted starch, seemed to confirm this view.

For both the glutinous and non-glutinous starches, the alkali numbers and viscosity records showed that sufficient iodine was adsorbed at the higher levels of concentrations to cause rupture of primary bonds near or within the surface of the granule as a consequence of the formation and decomposition of nitrogen triiodide.

For starches of both the No. 8 and No. 10 series, the viscosity records of the products after adsorption and removal of iodine were similar in form to the curves produced after solvent extraction. Gelatinization began at a lower temperature and proceeded more rapidly than that of the original starches. The decrease in viscosity during cooking was less and the increase during cooling was much more rapid. Also the ratio, w_2/w_1 , increased, indicating that the starch became more non-glutinous in character. The ratio, $(GS-w_2)/w_2 \times 100$, has been found, as the result of extensive work in this laboratory, to be the best indi-

cation available of the length of the paste formed. In all instances iodine treatment lowered this ratio, indicating a shorter paste. Thus it would seem that the iodine adsorption and removal, at least at the lower concentrations of iodine, served to alter the hydrogen bonding network on the surface of the granule. This allowed the granule to relax and thus acquire more structure. It also altered the degree of permeability of the surface to water which resulted in an effect closely approximating that produced by solvent extraction.

The samples of extracted non-glutinous starches, after adsorption and removal of iodine, began gelatinization at a higher temperature than the original starches. The rates were approximately the same, w_1 was lower, there was practically no decrease during cooking, the rate of increase during cooling was about the same, and w_2 was somewhat lower. From this it is seen that it required a higher temperature for the water present in the granule to do its required work. Also the paste was sequestered to a high degree, indicating that during the pasting process there was much of the granule which was not penetrated by the water. This could result from uneven strain in the granule.

The sample of glutinous starch resulting from adsorption at a concentration of 0.1 g iodine per 100 ml of solution, showed a higher value of w_1 and w_2 , after removal of the iodine, than did the original starch. Part of this was due to the effect of the methanol wash. However, there was an additional rise of w_1 which could only be a result of modification of the granule surface.

The glutinous extracted starch, after adsorption and removal of iodine, showed a pronounced decrease in both w_1 and w_2 , compared with the original starch. This decrease was much more than the corresponding decrease which occurred in the unextracted glutinous series. This could result from the opening of the surface by the solvent extraction, which if accompanied by no noticeable increase in structure, would allow the iodine to penetrate the granule surface more deeply. Thus, when the adsorbed iodine was allowed to react with ammonia, greater structural damage would occur as the result of rupture of primary bonds.

Measurements of alkali lability confirmed assumptions based on the amount of iodine adsorbed and on the viscosity curves of the various samples. Series No. 8 and No. 8E showed a steady increase in alkali lability as the quantity of adsorbed iodine increased. The No. 8 series ranged from 9.46 for the native starch to 10.55 for the sample adsorbed at a concentration of 2.4 g iodine per 100 ml of solution, and the 8E series ranged from 10.21 for the original to 11.27 for the sample adsorbed at the concentration of 2.4 g iodine per 100 ml of solution. The higher values of the solvent extracted series was expected since past work has shown solvent extraction alone causes a higher alkali number. It is presumed that the higher values for the samples of Nos. 8 and 8E, adsorbed at a concentration of 2.4 g iodine per 100 ml of solution, resulted from rupture of primary bonds with the formation of odd electrons which provided focal points for attack by alkali.

The No. 10 series followed closely the same trend as the No. 8 with the exception of the original No. 10 adsorbed at a concentration of 0.2 g iodine per 100 ml of solution, which had a slightly lower alkali number than the native starch. Its overall viscosity curve fell just slightly below that of the original. From this it was assumed that the concentration of 0.2 g iodine per 100 ml solution must have been the optimum concentration for this starch. At this concentration, sufficient modification was accomplished on the surface to increase its permeability to water, but at the same time to maintain its function of trapping the water at incipient gelatinization. The decrease in w_1 and w_2 that this sample showed over the native starch probably was due to the solvent extraction effect of the wash methanol.

The native glutinous starch had a higher alkali lability than the extracted starch--the reverse of the results obtained using a non-glutinous starch. This was caused by an increased availability for water as a result of solvent extraction which resulted in a lower alkali number.

It was concluded from results of this work and other experimental evidence that the surface of the starch granule must act as a valve. It must allow water to diffuse in and out of the granule until incipient gelatinization, when it must radically restrict the outward diffusion. If the surface is damaged or modified so that it can no longer act as a valve, the resulting paste has a great deal of body and is highly sequestered, indicating the water which entered the granule was not trapped and allowed to do its maximum work.

SUMMARY

Iodine adsorption capacities of glutinous and non-glutinous starches were determined. Both native starches and those modified by varying degrees of solvent extraction were used.

It was found that the adsorption capacities of the non-glutinous starches were decreased and those of the glutinous increased as the degree of solvent extraction increased.

Colors ranging from violet to yellow were obtained for the starch-iodide complexes, depending upon the type of starch and upon the degree of solvent extraction.

The effect of extraction with cold absolute methanol upon the pasting characteristics and alkali lability of glutinous and non-glutinous starches was determined. Cold extraction, in the case of the glutinous starch, was found to be nearly as effective as hot extraction.

The iodine present in the starch-iodide complexes was removed by reaction with ammonia and effects upon pasting characteristics and alkali lability were noted. It was found that if the amount of iodine adsorbed was kept low, the surface could be modified without extensive damage to the gross structure of the granule.

The viscosity of the samples decreased as the amount of iodine present in the sample before reaction with ammonia increased. This indicated that primary bonds were broken at the higher levels of iodine concentrations used.

The alkali numbers of the samples steadily increased as the amount of iodine in the starch iodide complexes increased. It was assumed from this that the breakage of primary bonds, which occurred with the higher concentrations of iodine, resulted in free radicals which reacted with the alkali.

It was concluded that the surface of the starch granule functions as a valve. At incipient gelatinization this valve action must restrict radically the outward diffusion of water from the granule if the maximum viscosity is to be obtained.

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SOME EFFECTS OF SURFACE MODIFICATION
OF STARCH GRANULES BY IODINE

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The primary purpose of this problem was to study the relative importance of the surface to the gross structure of the starch granule through modification of the surface of the granule, and studying the effects of such modification by means of viscosity behavior and alkali lability. It was further the purpose of this work to study the effects of such modification upon various types of starches, both native and those modified by various degrees of solvent extraction, with regard to the amount of iodine adsorbed, viscosity, and alkali lability.

The method of attack chosen was the well-known starch-iodine reaction. Iodine was adsorbed on and into granular starch from an iodine solution to form the starch-iodide complex, after which the iodine in the complex was removed by reaction with ammonia.

It was found that the adsorption capacities of the non-glutinous starches were decreased and those of the glutinous increased as the degree of solvent extraction increased.

Colors ranging from violet to yellow were obtained for the starch-iodide complexes, depending upon the type of starch and upon the degree of solvent extraction.

The effect of extraction with cold absolute methanol upon the pasting characteristics and alkali lability of glutinous and non-glutinous starches was determined. Cold extraction in the case of the glutinous starch was found to be nearly as effective as hot extraction.

The adsorbed iodine in the starch-iodide complexes was reacted in situ with ammonia to form nitrogen tri-iodide. This nitrogen tri-iodide which is highly unstable at room temperature is presumed to have decomposed violently and in so doing modified the surface and gross structure of the starch granule to a degree depending upon the location and amount of adsorbed iodine. It was planned that the amount of adsorbed iodine be kept small so that the resulting modification would be limited primarily to the surface without causing extensive damage to the gross structure of the granule.

It was found that the viscosity of the samples decreased with increased iodine present in the sample before reaction with ammonia. This indicated that primary bonds were broken at the higher levels of iodine concentrations used.

The alkali numbers of the samples steadily increased as the amount of iodine in the starch-iodide complexes increased. It was assumed from this that the breakage of primary bonds, which occurred with the higher concentrations of iodine, resulted in free radicals which reacted with the alkali.

It was concluded that the surface of the starch granule functions as a valve. At incipient gelatinization this valve action must restrict radically the outward diffusion of water from the granule if the maximum viscosity is to be obtained.